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Permeability and Corrosion Resistance of Reinforced Sulfur Concrete

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UNITED STATES DEPARTMENT OF THE INTERIOR

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UNIT OF MEASURE ABBREVIATIONS USED IN THIS REPORT

°C	degree Celsius	lb	pound
cm	centimeter	mA	milliampere
cm^2	square centimeter	mL	milliliter
cm/s	centimeter per second	mm	millimeter
cm^2/s	square centimeter per second	mV	millivolt
cm^3/s	cubic centimeter per second	Pa	Pascal
		Pa/cm	pascal per centimeter
$(cm^2/V)/s$	square centimeter per volt per second	Pa·s	pascal second
		pct	percent
°F	degree Fahrenheit	psi	pound (force) per square inch
ft	foot		
gal	gallon	s	second
$(g/cm^2)/s$	gram per square centimeter per second	V	volt
		V/cm	volt per centimeter
h	hour	V dc	volt, direct current
in	inch	wt pct	weight percent
L	liter		

PERMEABILITY AND CORROSION RESISTANCE OF REINFORCED SULFUR CONCRETE

By W. R. Wrzesinski[1] and W. C. McBee[2]

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ABSTRACT

This report presents the findings from a 1-yr Bureau of Mines program in which sulfur concrete reinforcing materials were tested and evaluated to determine their resistance to corrosion. It also summarizes the permeation characteristics of sulfur concrete and the exemplary performance of precast, reinforced sulfur concrete structures in various industrial environments.

The Bureau is furthering the development of sulfur concrete technology as part of a larger effort to find uses for the Nation's plentiful sulfur resources in construction materials. Sulfur concrete is a corrosion-resistant material that can be used in acid and salt environments where conventional materials fail. Penetration of corrosion-inducing agents is minimized because of the low permeation characteristics of sulfur concrete.

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INTRODUCTION

Sulfur is one of the most abundant elements, ranking 13th in amount in the Earth's crust and occurring in both elemental and combined states. The United States is the world's leading producer of sulfur (1).[3] Research by Southwest Research Institute in 1968 indicated the potential use of sulfur as a construction material (2). In 1972, the Bureau of Mines initiated a research program directed toward utilization of sulfur, which was projected to be a surplus material through the year 2000 (3). Research has centered on use of sulfur as a construction material to replace energy-intensive materials such as asphalt and cement.

As part of its sulfur research program, the Bureau has been active in the development of sulfur concrete technology. Using a chemically modified sulfur mixed with suitable mineral aggregates, the Bureau previously produced sulfur concrete construction materials that are resistant to corrosion by acids and salts (4). Sulfur concrete materials exhibit excellent mechanical properties when compared to portland cement concrete and have shown no signs of strength loss or degradation after more than 5 yr of industrial testing in over 50 corrosive environments (5). Typical mechanical properties of sulfur concrete are shown in table 1. Each year the United States sustains billions of dollars in damage losses due to corrosion of reinforced concrete structures. Recent reports indicate that current losses to the U.S. economy as a result of corrosion total about $140 billion annually (7). Currently, first-generation sulfur concretes are being precast or installed directly in industrial plants where portland cement concrete materials fail from acid and salt corrosion. Typical installations are floors, sumps, electrolytic cells, drainage ditches, sidewalls, and foundation for columns and pumps.

A specific problem with portland concrete materials is the premature corrosion of reinforcing steel, which severely affects the structural integrity of highway bridge decks. The major factor contributing to these corrosion problems is the chloride ion (which infiltrates into the concrete as a result of road de-icing and marine environments) and its role in destroying the passivity of iron in a concrete environment (8). Technical advisors to the Strategic Highway Research Program (SHRP) estimate that 253,196 of the more than 500,000 bridges in the United States were structurally deficient before 1982 and that more than $48.9 billion will be required to repair or replace these deficient bridges (9). Additionally, premature corrosion of reniforcement steel is a substantial contributor in some 3,300 bridges which become deficient each year (10).

Concrete with low permeability impedes penetration of corrosive agents (chloride and sulfate ions, oxygen, and water), thus reducing the corrosive effects of these agents.

This report compares the permeation characteristics of sulfur concrete with conventional materials and illustrates the resistance of sulfur concrete reinforcing materials to corrosion.

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[3]Underlined numbers in parentheses refer to items in the list of references at the end of this report.

TABLE 1. - Strengths of typical sulfur concretes

Aggregate[1]	Sulfur cement, pct	Strength, psi		
		Compressive	Tensile	Flexural
Quartz......................	16	7,720	1,040	1,440
Limestone....................	18	8,710	1,050	1,720

[1]3/8-in dense graded.

Source: McBee (6, p. 7).

ACKNOWLEDGEMENT

THEORY OF PERMEATION

The flow of the chloride or sulfate ion, along with the flow of other fluids and ions through concrete, occurs by a number of different mechanisms, depending upon the initial state of the concrete, the nature of the permeating substances, temperature, and pressure. The movement of water in porous materials is characterized by Rose (11) into seven distinct stages, as shown in figure 1. After the initial absorption and surface diffusion in stage 1, water vapor movement is controlled by diffusion in stage 2.

Diffusion is mathematically expressed by Fick's first law (12):

$$J = - D \, (dc/dx),$$

where J = mass flux, $g/cm^2 s$,

D = diffusion coefficient, cm^2/s,

and dc/dx = mass concentration gradient, $(g/cm^3)/cm$.

Stage 1: Adsorption and surface diffusion

Stage 2: Vapor diffusion

Stage 3: Film transfer

Stage 4: Surface creep plus vapor diffusion

Stage 5: Partially saturated liquid flow

Stage 6: Liquid flow

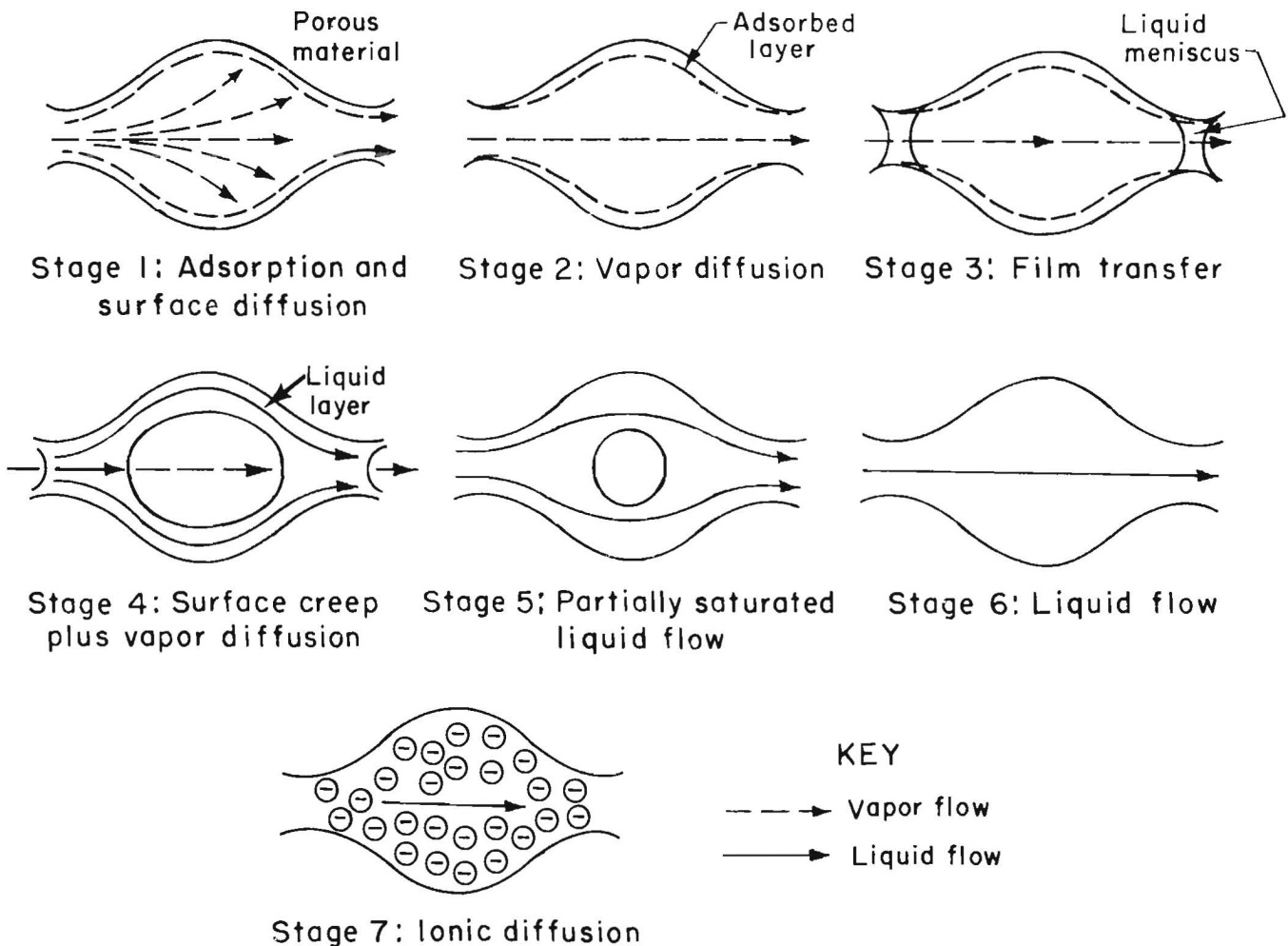Stage 7: Ionic diffusion

KEY

– – –▶ Vapor flow

——▶ Liquid flow

FIGURE 1.—Movement of water through porous material (after Rose, 11).

Chloride and sulfate ions cannot transfer by way of vapor phase diffusion; however, a relative permeability may be calculated from the measurement of water vapor transmission.

With increased water vapor, water begins to condense within the capillary spaces. A pressure differential then occurs across the liquid meniscus in the capillary (stage 3 in figure 1). This pressure differential in turn induces flow through the capillary, the rate being governed by Washburn's equation (13):

$$v = (rV/4dn) \cos \theta$$

where v = flow rate, cm/s,

           r = capillary radius, cm,

           V = surface tension, Pa/cm,

           d = depth of penetration, cm,

           θ = contact angle,

and n = fluid viscosity, Pa·s.

Once the pore system is completely saturated, water may flow as a fluid. In materials having very finely divided pores, however, significant flow will occur only under high pressure heads. The rate of fluid flow is essentially proportional to the pressure drop per unit length given by Darcy's Law (12):

$$Q = -KAdH/L,$$

where Q = volumetric flowrate, cm^3/s,

           A = area, cm^2,

          dH = fluid head, cm,

           L = path length, cm,

and K = permeability constant, cm/s.

The chloride and sulfate ion, and other ionic species, can move slowly through free water within the concrete pore structure by diffusion in stages 3 and 4 (figure 1). The flow increases through stages 5 and 6 until finally, in stage 7, which represents the fully saturated state, ions will travel at a faster rate and ionic diffusion will be the most effective.

A special case of diffusion occurs when an electric potential is applied across an electrolytic solution contained within a porous material; the ions are transported towards the electrode of opposing sign (14). Ionic mobility is given by the following equation:

$$u = x/(t(dE/dx)),$$

where u = ionic mobility, $(cm^2/V)/s$,

           X = distance, cm

           t = time, s

and dE/dx = electric field strength, V/cm.

RAPID DETERMINATION OF CONCRETE PERMEABILITY

A technique for rapid determination of the ion permeability of portland cement concrete, developed by the Portland Cement Association, was used to determine the chloride, sulfate, and water permeabilities of portland cement concrete and sulfur concrete (15). Since electrical resistivity of concrete decreases with increasing chloride ion concentration, a measure of the increase in current with time can be correlated with the amount of chloride entering the concrete. Extensive evaluations of the rapid determination technique have indicated that the rapid test results correlate quite well with standard ponding tests and long-term outdoor exposure studies of concretes of various permeabilities (16).

Samples of portland cement concrete and sulfur concrete were cast in 3-in-diam by 6-in-high cylindrical molds. Portland cement concrete was formulated using 3/8-in quartz coarse aggregate, a maximum water-to-cement ratio of 0.5, and 5 bags of cement (470 lb) per cubic yard of concrete. Sulfur concrete consisted of

19 pct modified sulfur cement and 81 pct 3/8-in maximum size, dense-graded quartz aggregate. The quartz aggregate was clean, sound, and free from swelling constituents. The specific gravity of the aggregate was 2.8, and its moisture absorption and acid dissolution were both less than 1 pct. The dense-graded aggregate used for sulfur concrete contained 55 wt pct of minus 3/8-in crushed quartz, 40 wt pct of minus 1/8-in crushed quartz, and 5 wt pct of minus 200-mesh silica flour. A dense-graded quartz aggregate was used for the portland cement concrete; however, the minus 200-mesh fraction was eliminated. Aggregate size distribution follows a Fuller maximum density curve (6). A diamond saw was used to cut the 3-in-diam samples into 2-in-thick sections. Samples were sawed slowly to obtain a smooth, clean surface, and any burrs were removed with a belt sander. A summary of the rapid technique for permeation determination is presented in the following paragraphs in three steps: sample preparation, testing of the specimen, and interpretation of results (15).

Preparation of the concrete specimens consisted of applying an impermeable epoxy coating onto the sides of each sample (such as DIBA 6010 resin 1XV-225 hardener[4] at a 1:1 ratio by weight) and vacuum saturation of each sample with deaerated water.

Testing of the specimens involved first mounting the prepared specimen into the applied voltage cell as shown in figure 2. Solutions were then added to the cell according to which ion permeability was being tested. For chloride permeability, the left side (-) of the cell was filled with sodium chloride and the right side (+) of the cell with $0.3N$ sodium hydroxide. In testing for sulfate permeability, a 3 pct sulfuric acid (-) solution was used in conjunction with a 1 pct sulfuric acid (+) solution, and a 3 pct potassium bisulfate (-) solution was used with a 1 pct potassium bisulfate (+) solution. In determining the water

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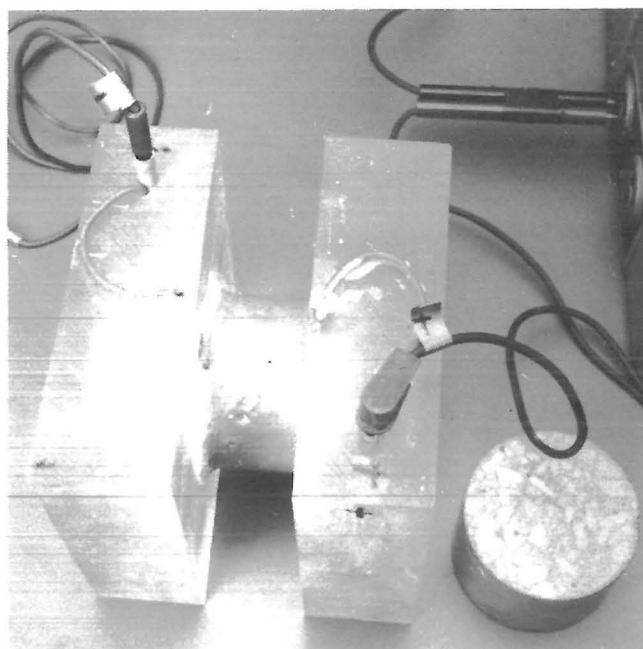[4]Reference to specific products does not indicate endorsement by the Bureau of Mines.

FIGURE 2.—Specimen mounted in applied voltage cell.

permeability, distilled water was used in both cells. Finally, a voltage of 60.0 V dc was applied (fig. 3), and current was measured every 1/2 h for the 6-h test period.

Interpretation of the results was facilitated through construction of a plot for each test of current (in amperes) versus time (in seconds) and integration of the area underneath the curve in order to obtain the charge passed during the 6-h test period (in ampere-seconds, or coulombs). While conventional integration techniques such as planimetry or paper weighing could have been used, a programmable hand-held calculator was used to numerically integrate the area underneath the current-versus-time plot.

Table 2 shows the relationship between chloride permeability, the corresponding amount of charge passed (in coulombs), and the type of concrete which typically renders the given results. This table was developed from data on 3.75-in-diam by 2-in-thick core specimens taken from laboratory slabs prepared from various types of concretes. These data showed good correlation with 90-day ponding test results on companion slabs cast from the same concrete mixes (16). The effects of such variables as aggregate type and
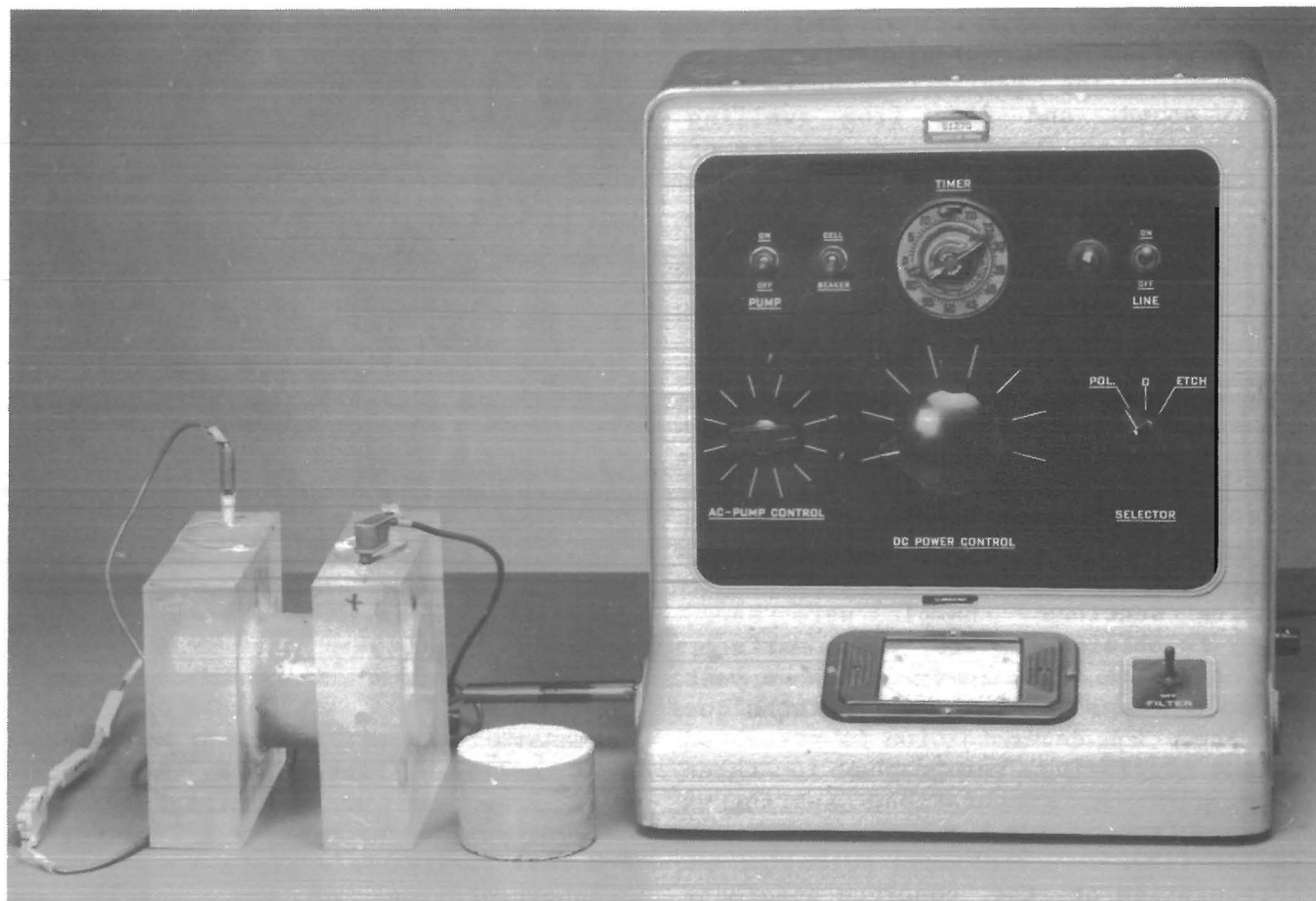
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FIGURE 3.—Power source attached to applied voltage cell.

TABLE 2. – Data used to interpret applied voltage test results (table 3)[1]

Chloride permeability	Charge passed, C	Type of concrete which typically renders results given in columns 1 and 2
High.....................	>4,000	High water-to-cement ratio (>0.6).
Moderate.................	2,000-4,000	Moderate water-to-cement ratio (0.4-0.5).
Low......................	1,000-2,000	Low water-to-cement ratio (<0.4).
Very low.................	100-1,000	Latex modified; internally sealed.
Negligible..............	<100	Polymer impregnated or polymer concrete.

[1]Based on applied voltage tests using various types of concrete.

size, cement content and composition, density, and other factors have not been evaluated. It is recommended that persons using the procedures described here prepare a set of concrete specimens representing each local material source and use them to establish a similar table of correlation between charge passed and known chloride permeability for each specific concrete mixture.

A plot of current versus time for the sulfur concrete and portland cement concrete is shown in figure 4. (In figures 4 and 5, SC indicates sulfur concrete, and PCC indicates portland cement concrete.) The sulfur concrete specimens showed negligible current passage during the 6-h test period. The portland cement concrete test specimens, however, showed current passage of greater than 40 mA in all environments tested. The highest amperage through a specimen for the duration of the test was recorded for the chloride ion (NaCl), through the portland
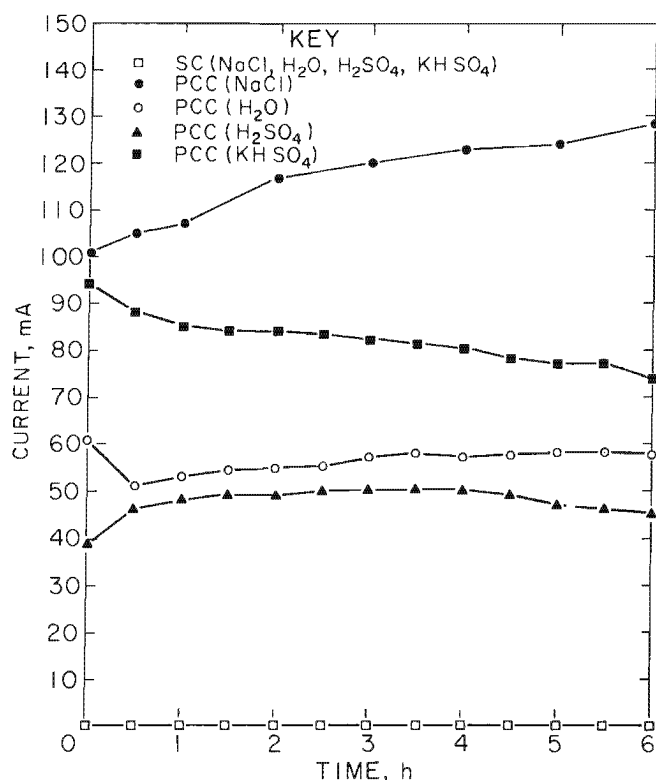
FIGURE 4.—Current versus time for various concrete samples tested at 60.0 V dc.

FIGURE 5.—Temperature rise versus time for various concrete samples tested at 60.0 V dc.

cement concrete. Current passage through this concrete was also high with the other solutions tested, clearly demonstrating the higher permeability of portland cement concrete.

The temperature change of the applied voltage cell versus time is illustrated in figure 5. The sulfur concrete specimens showed little temperature change throughout the test duration for all of the environments tested. However, the portland cement concrete specimens showed a constant temperature gain during the entire test period and in all environments tested.

The applied voltage test results are shown in table 3. Interpretation of these results can be facilitated by using the values listed in table 2. Sulfur concrete test specimens performed as well as other polymerized materials, with values for charge passed during the 6-h test of less than 100 C in all cases. Sulfur concrete test specimens exhibited superior performance by demonstrating negligible permeability in all
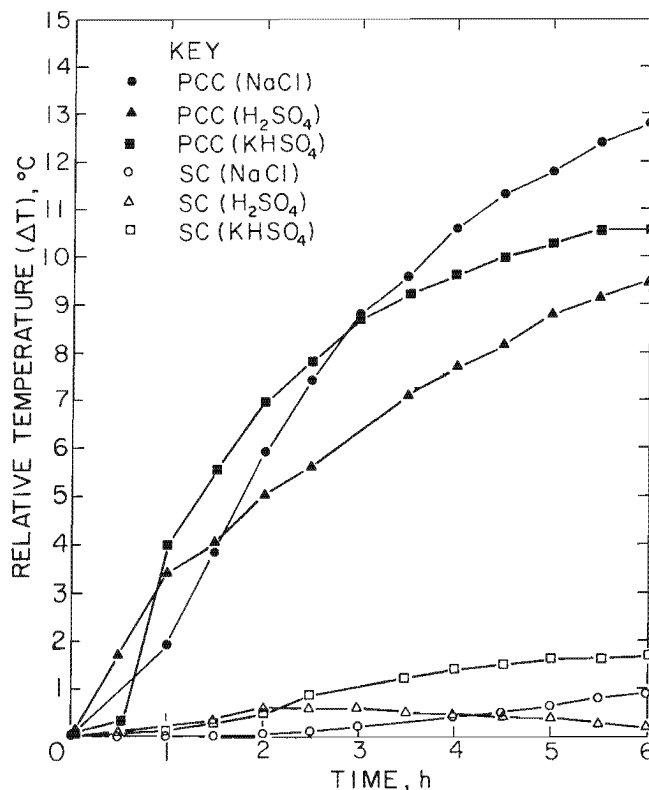
TABLE 3. - Applied voltage test results
(Charge passed in 6-h, coulombs)

Environment	PCC	SC
Sodium chloride.............	2,538	0.72
Potassium bisulfate.........	1,782	0
Sulfuric acid...............	986	0
Distilled water.............	1,231	0

PCC   Portland cement concrete.
SC   Sulfur concrete.

environments tested, while portland concrete test specimens showed much higher permeability in all environments tested.

Confirmation testing of sulfur concrete specimens was conducted by the Federal Highway Administration (FHWA) at its Turner-Fairbank Highway Research Center in McLean, VA. Independent results obtained by the FHWA support the observations and test results reported here. As in this research, the FHWA test results showed that sulfur concrete has negligible permeability.

LONG-TERM CORROSION TESTING

Resistance of sulfur concrete reinforcing materials to corrosion was determined for a 1-yr period. Measurements were made in accordance with American Society for Testing and Materials (ASTM) method C876-80, "Half Cell Potentials of Reinforcing Steel in Concrete" (17). Sulfur concrete test samples were cast into 3- by 3- by 14-in beams with reinforcing steel (No. 4) centered in the casting with a minimum side wall clearance of 1 in, as shown in figure 6. The corrosion test equipment and testing of the specimens in progress is illustrated in figure 7.

Data were obtained for sulfur concrete reinforced with (1) uncoated steel (control), (2) epoxy-coated steel, and (3) steel dip-coated with polyvinyl chloride (PVC) plastic. Samples were immersed in three environments: water, 5 pct sodium chloride, and 5 pct sulfuric acid. At least 3 samples of each type were tested in each solution. Separate tanks were used for each solution, and a saturated calomel electrode (SCE) was used as a reference electrode. The performance of each type of sample in each environment was evaluated over the 1-yr test period.

Table 4 shows the various categories used for interpretation of the test data (18). These categories were used to interpret the graphs shown in figure 8.

All three types of sulfur concrete samples tested in 5 pct sodium chloride showed a resistance to corrosion during the first year of testing. Figure 8 illustrates corrosion activity in a 5 pct sulfuric acid environment and in water. In the acid environment, the samples with
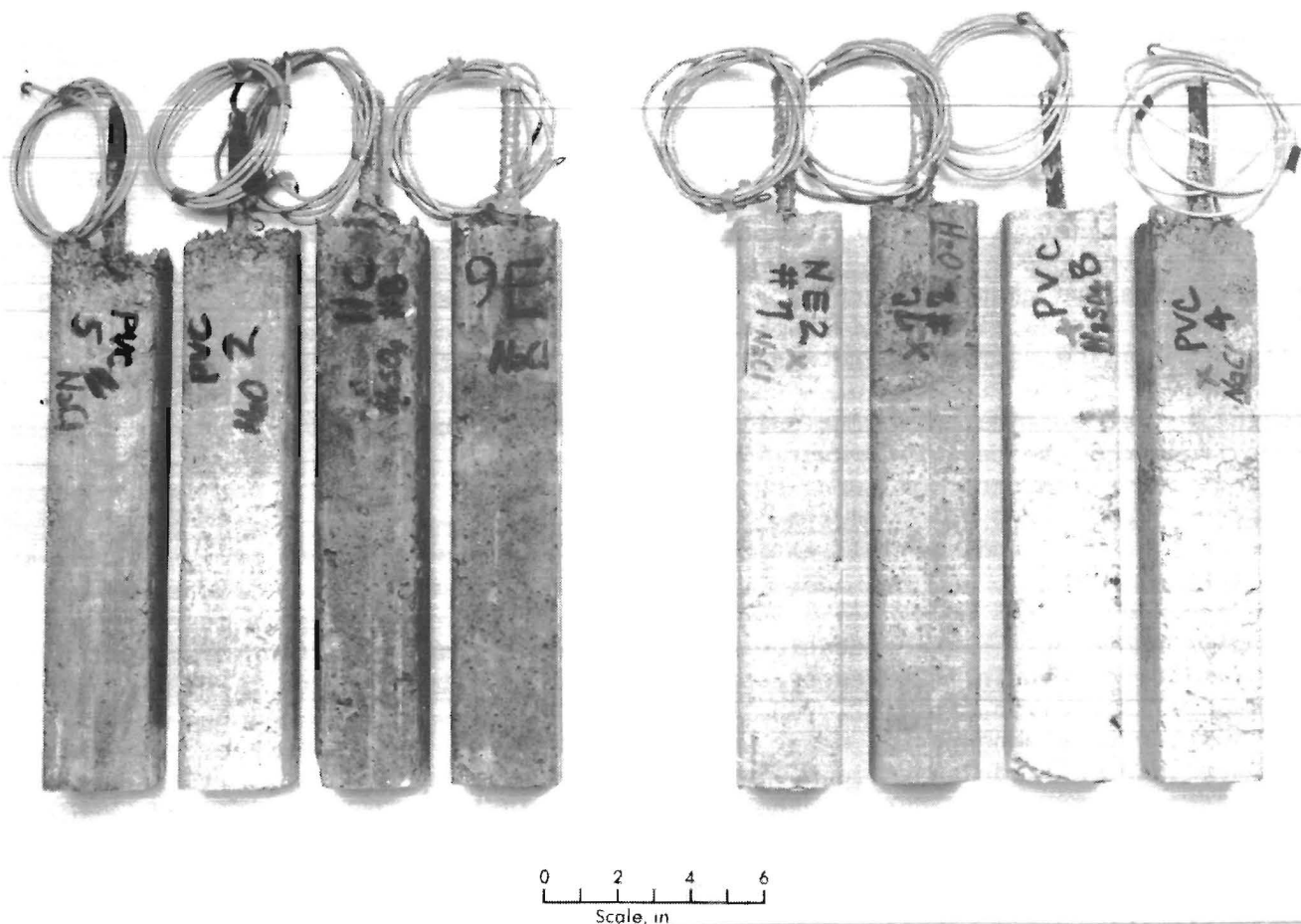

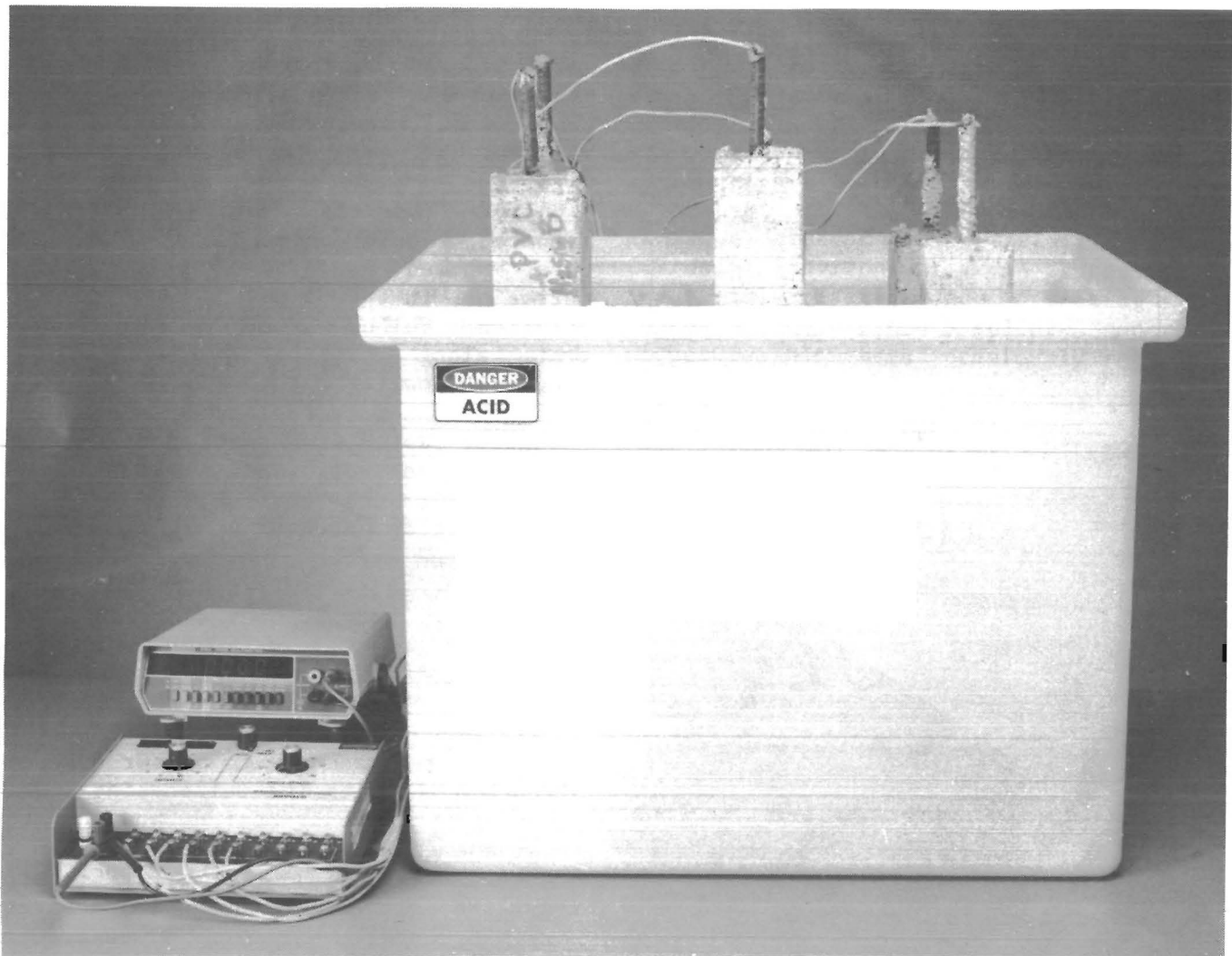FIGURE 6.—Long-term corrosion test specimens.

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FIGURE 7.—Long-term corrosion test apparatus.

TABLE 4. – Categories used to interpret long-term corrosion test results (figure 8)

E corrosion (V vs V_{SCE})	Condition of steel
<-0.22................	Passive.
>-0.22 but <-0.27....	Active or passive.
<-0.27................	Active.

Source: Wheat (17).

uncoated steel (control) and epoxy-coated steel showed no corrosion activity for the 1-yr period of testing, while the samples with PVC-coated steel showed a much higher potential for corrosion activity within the first 6 to 8 months of testing. Conversely, in water, the sulfur concrete samples reinforced with PVC-coated steel showed the best resistance to corrosion. Samples reinforced with epoxy-coated rebar showed probable corrosion activity after only 6 months of testing.

Results indicate that the uncoated reinforcing steel was least affected in all the environments tested. One possible explanation for this may be that a small imperfection in the epoxy or PVC coatings provided a means by which corrosive materials could infiltrate and remain in contact with the steel (trapped between the coating and the steel), thus creating accelerated corrosion activity. A higher potential for accelerated corrosion of both epoxy- and PVC-coated reinforcing steel is supported by the data
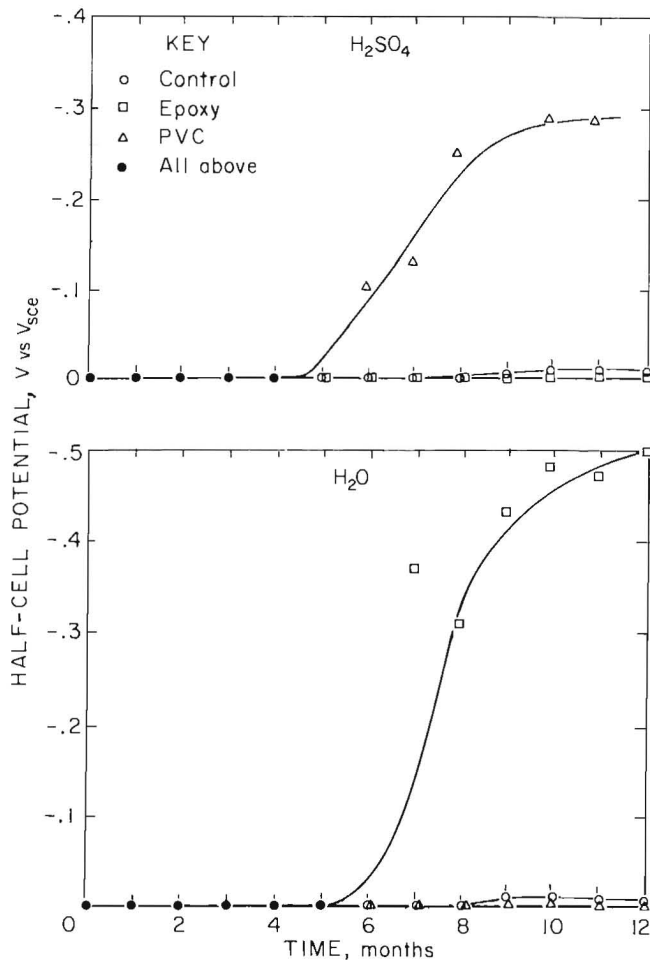
FIGURE 8.—Half-cell potential versus time for sulfur concrete samples tested in 5 pct sulfuric acid and in water.

presented in figure 8, which clearly shows rapid change from a passive state to an active state for two of the samples with coated steel.

Microanalysis of sulfur concrete samples after testing in each environment was undertaken to determine the composition of corrosion products at the steel-concrete interface and to determine the extent of corrosion that occured during the test period. Samples were coated with carbon to make them conductive and then analyzed by using a scanning

electron microscope (SEM) equipped with an energy-dispersive X-ray system (ZAP) and electron microproble. Results of this microanalysis are summarized below. These results correlated well with the measured half-cell potentials shown in figure 8.

Sulfur concrete samples containing uncoated, epoxy-coated, and PVC-coated rebar showed no evidence of chloride corrosion in the 5 pct sodium chloride solution. Sulfur was observed to concentrate along the rebar surface in all samples; however, the epoxy and PVC remained intact in the coated samples.

Samples tested in water showed a higher potential for corrosion for the sample with epoxy-coated reinforcing steel. ZAP analysis, conducted on the sample with epoxy-coated steel, showed the highest sulfur concentration in the corrosion layer next to the rebar (table 5). The most significant results of this stoichiometric analysis were that iron sulfide was not present within this entire (inner) oxide layer, demonstrating that sulfur present in sulfur concrete did not react with the reinforcing steel.

Samples with epoxy-coated and uncoated rebar showed no significant corrosion in 5 pct sulfuric acid; however, PVC-coated rebar showed increased corrosion activity within 6 months. Sulfur was measured by ZAP analysis under the PVC coating in the form of both iron sulfide and a smaller portion of iron oxide. Sulfur again concentrated along the rebar surface of all of the samples.

TABLE 5. – ZAP[1] analysis of epoxy-coated steel surface tested in water, weight percent

	Si	Fe	S
Outer oxide layer.............	27	61	12
Oxide layer...................	23	10	67
Metal surface.................	4	93	3

[1]Energy-dispersive X-ray system.

INDUSTRIAL APPLICATIONS OF SULFUR CONCRETE

Beginning in 1977, the Bureau of Mines, in conjunction with The Sulphur Institute, initiated a cooperative industrial testing program to test sulfur concrete in industrial corrosive environments. Components such as tiles, slabs, tanks, and pump foundations were precast and subsequently transported and placed in industrial plants. Mechanical strength test specimens were also placed onsite so that material properties could be tested after the specimens were subjected to particular corrosive environments. Uncoated reinforcing steel was used in practically all of the precast units, with no apparent corrosion problems to date. Figure 9 shows the use of rebar in a precast unit, and figure 10 shows a finished precast unit installed in a corrosive environment. A summary of industrial performance testing of precast, reinforced sulfur concrete structures has been previously reported (5).
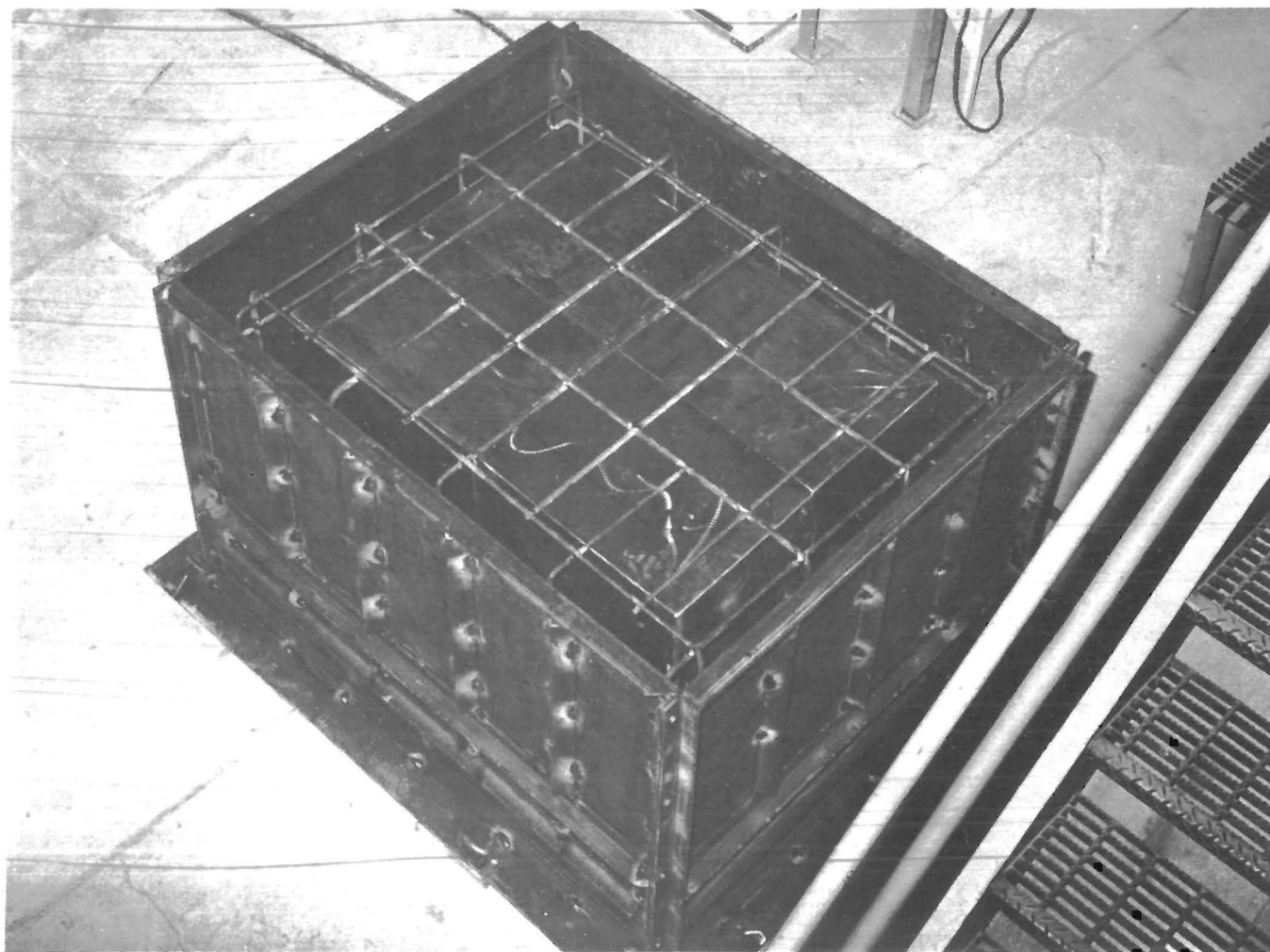

FIGURE 9.—Use of rebar in fabricating a sulfur concrete precast unit.

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FIGURE 10.—Sulfur concrete sump unit in industrial corrosive environment.

The durability and performance life of sulfur concrete is being established. The oldest corrosion-resistant sulfur concrete materials being evaluated are components in sulfuric acid solutions and copper electrolytic solutions. These units have shown no evidence of corrosion or deterioration after 7 yr of service. Since sulfur concrete is a relatively new material, longer periods of testing will be necessary to fully establish its service life.

CONCLUSIONS

Sulfur concrete is a corrosion-resistant material that demonstrates superior performance when properly used in environments where conventional materials fail. Permeation, corrosion, and industrial testing have yielded the following conclusions:

Sulfur concrete has improved resistance to chloride and sulfate ion permeability, compared to portland cement concrete.

Sulfur concrete can be successfully substituted for portland cement concrete to construct many precast and cast-in-place corrosion-resistant structures.

Uncoated reinforcing steel outperforms both epoxy-coated and PVC-coated reinforcing steel in sulfur concrete specimens tested in 5 pct sodium chloride, in 5 pct sulfuric acid, and in water.

Sulfur concrete is completely compatible with uncoated reinforcing steel for use in the environments tested.

Precast industrial testing units which contain uncoated reinforcing steel have provided excellent performance and extended service life in a variety of corrosive environments.

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